there was obtained a total of 2 g. (24% of the theoretical amount) of the desired amino acid. The product melted at 272° (uncorr.) and the picrolonate darkened at 176–179° and melted at 179–180°. Barger and Coyne report the two melting points as 281° and 178°, respectively.

Anal. Subs., 0.1584, 0.1080: $BaSO_4$, 0.2521, 0.1692. Calcd. for $C_5H_{11}O_2NS$ S, 21.5. Found: S, 21.84, 21.51.

Summary

A new synthesis of methionine, γ-methylthiol-α-amino-*n*-butyric acid, has been described.

URBANA, ILLINOIS

COMMUNICATIONS TO THE EDITOR

THE SPECTROSCOPIC DETERMINATION OF THE DECOMPOSITION PRODUCTS OF ORGANIC COMPOUNDS. BENZENE IN THE ELECTRODELESS DISCHARGE

Sir:

An interesting and beautiful phenomenon is observed if benzene vapor at about 0.1-mm. pressure is subjected to the electrodeless discharge. At first a greenish glow appears near the walls of the flask adjacent to the wires. Almost immediately this spreads through the entire flask, turns red, and is extinguished by the resultant decomposition and recombination to form a solid hydrocarbon. This stops the discharge by lowering the pressure. After 40 discharges of this type the walls of the flask are found to be covered by a thin, transparent, amber-colored deposit.

However, if benzene vapor is admitted at just the rate to keep the pressure at a value suitable for the discharge, the glow persists and the accompanying decomposition and synthesis proceed continuously for an hour or more. Thus several thousand liters of the vapor are completely decomposed and quantitatively converted into a reddish-brown flaky powder. This has the same composition as benzene, according to the analysis of Dr. I. E. Muskat, but a much higher molecular weight. The formula is thus $(CH)_n$.

The spectrum, (Fig. 1) indicates that the benzene molecules rapidly decompose into molecules of C_2 and CH, and atoms of C^+ and H. Thus the 5 groups of Swan bands, and a considerable number of the other C_2 bands, as discovered by Deslandres and D'Azambuja, were found, as well as the λ4300 and λ3900 bands of CH. In addition the first four lines of the Balmer series of hydrogen, and the line spectrum of C^+ appeared.

The C_2, CH, C^+ and H seem to combine completely to form the reddish-brown hydrocarbon, as evidenced by the fact that several thousand liters of benzene vapor decompose without giving enough gaseous residue to raise the pressure sufficiently to extinguish the discharge.

The spectra were photographed by Hilger quartz spectrographs, and a

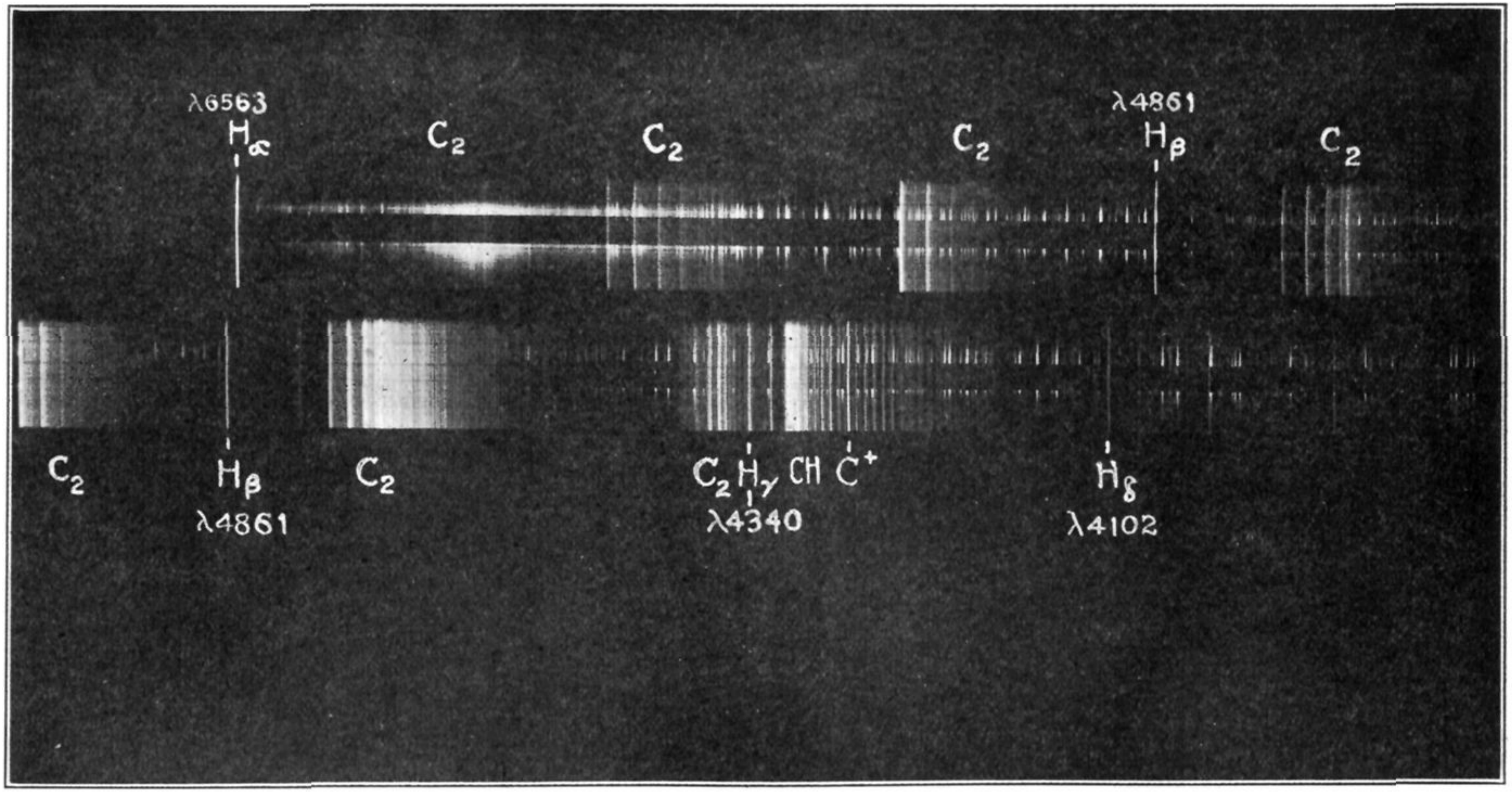

Fig. 1.—Spectrum of molecules of C_2 and CH, with the first four lines of the Balmer spectrum of hydrogen, together with lines of the C^+ spectrum, as obtained from the decomposition products of benzene in the electrodeless discharge, with a frequency of 1000 kilocycles per second.

Steinheil glass spectrograph of high dispersion. The apparatus (Fig. 2) consisted of a liter flask with a quartz window, connected with a gage and vacuum pump, and surrounded by 6 coils of wire from a 25,000-volt transformer and a condenser of 0.02 microfarads capacity. This stores about 1 calorie of energy at 25,000 volts. The benzene is dried with great care before it is put into the apparatus, and its vapor passes through a tube (D) of phosphorus pentoxide just before it enters the flask.

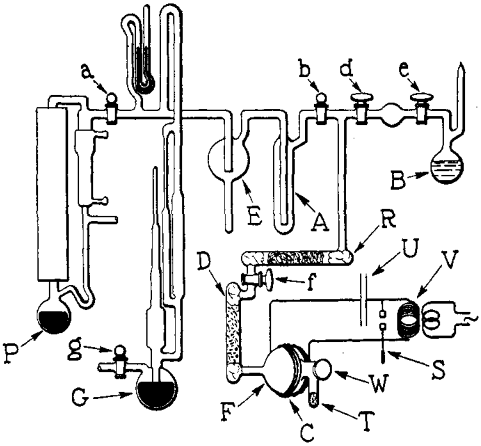

Fig. 2.—Apparatus for the decomposition of organic vapors.

The frequency of the discharge was 1000 kilocycles per second. The pressure at which the discharge acts rises with increasing distance between the terminals of the spark gap. Thus with a 1.5-mm. spark gap the maximum pressure is 0.05 mm., while with a gap of 6 mm. the maximum pressure is 0.25 mm.

In so far as the spectra found are excited by electronic collisions, the velocities of the electrons range between 1.9 and 3.6 volts or between 0.85×10^8 and 1.14×10^8 cm. per second. The limits probably extend farther in each direction. The intermediate products in the decomposition of other organic compounds, such as methane, acetylene, phenol, etc., will be determined, since the spectroscopic method is one of great convenience and usefulness.

George Herbert Jones Laboratory
University of Chicago
Chicago, Illinois

William D. Harkins
David M. Gans

Received May 2, 1930
Published June 6, 1930

THE HEAT OF FORMATION OF MOLECULAR OXYGEN

Sir:

The reported values for the heat of formation of molecular oxygen range from 162,000 to 110,000 calories. These values have all been determined by indirect methods. A direct determination of the heat of formation of molecular oxygen has now been obtained using an apparatus essentially the same as that of Bichowsky and the author[1] for hydrogen. This apparatus employs the method of Weide and Bichowsky[2] for determining the

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[1] Bichowsky and Copeland, This Journal, **50**, 1315 (1928).

[2] Weide and Bichowsky, *ibid.*, **48**, 2529 (1926).

percentage dissociation of a diatomic gas. Atomic oxygen was produced by means of the electrodeless discharge. The recombination took place on the surface of a calorimeter coated with palladium black. It has been shown that water vapor is necessary for the production or at least for the maintenance of the atomic gas.

In the preliminary experiments reported at this time 16 to 25% dissociation was realized at a distance of 10 cm. from the discharge bulb at pressures of 0.1 to 0.2 mm. of mercury. The validity of the application of Knudsen's formula for the measurement of the percentage dissociation at these pressures has been established experimentally by measuring the rate of flow of oxygen through the orifices at the two limiting pressures and also the rate of flow of hydrogen at one pressure lying between these limits. The heat of formation of molecular oxygen as given by these experiments is 7.2 (± 0.2) volts or 165,000 (±5000) calories per gram molecular weight. It is to be noted that although this value is in good agreement with some of the older values, it is considerably higher than those reported within the last year. As it is quite possible that the presence of metastable atoms is giving too high a value, further experiments are now in progress using different pressures and different lengths of path, under which conditions the average life of a metastable atom should be changed. It is hoped in this manner either to prove the absence of metastable states or at least to be able to correct for their excess energy should they be present.

JEFFERSON PHYSICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
L. C. COPELAND[3]

RECEIVED MAY 3, 1930
PUBLISHED JUNE 6, 1930

ELECTRO-DEPOSITION OF METALLIC BERYLLIUM

Sir:

We wish to announce that as a result of work carried on for a number of years we have been able to obtain metallic beryllium by the electrolysis of solutions of beryllium salts in various organic and inorganic non-aqueous solvents. Although the solutions of beryllium salts in substituted ammonias give deposits of metal, the most satisfactory solvent is liquid ammonia itself either alone or with the addition of salts or other compounds which lower the vapor tension of the solution and increase the solubility of beryllium salts. Thus the metal has been prepared from solutions which may be electrolyzed at room temperature. The metal obtained by these electrolyses is so pure that it is insoluble in even the strongest acids unless the metal is in contact with a more electro-negative metal such as platinum. Under the microscope the metal is seen to be crystalline.

Hitherto all attempts to dehydrate beryllium salts have yielded basic

[3] National Research Fellow in Chemistry.

salts, due to partial hydrolysis. We have discovered that beryllium salts may be dehydrated by heating in fused ammonium salts. Beryllium salts so dehydrated may be electrolyzed in liquid ammonia solution without removing the excess ammonium salts and yield metallic beryllium.

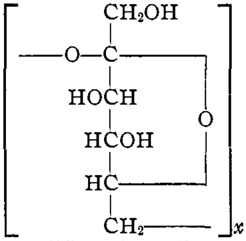
THE MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
HAROLD SIMMONS BOOTH
G. G. TORREY

RECEIVED MAY 16, 1930
PUBLISHED JUNE 6, 1930

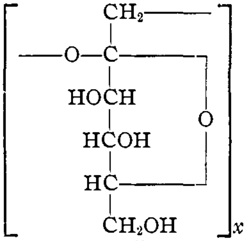
THE STRUCTURE OF "GUM LEVAN"

Sir:

"Gum Levan," formed by the action of *Bacillus mesentericus* on cane sugar, has been definitely identified by hydrolysis, acetylation and methylation experiments conducted in this Laboratory as a polymerized anhydrofructofuranose, the linkages being at positions 2 and 6 of the fructose sugar chain, as compared with the 1,2-linkage in the case of inulin. It can be prepared in a pure state, free from nitrogen and ash, by the action of the enzyme isolated from the organism.



"Gum Levan"



Inulin

When submitted to the action of *Bacillus xylinum* it yields a new product, apparently more highly polymerized, which is at present under investigation.

Methylation of "levan" yields a trimethyl derivative which on hydrolysis gives a new crystalline 1,3,4-trimethylfructofuranose, m. p. 63°, the first crystalline γ-sugar to be isolated. Its constitution is confirmed by its inability to form an osazone, transformation to tetramethyl-γ-fructose, and oxidation by nitric acid to yield a dibasic dimethyl lactol acid. The diethyl ester of the latter on methylation and treatment with dry ammonia gives a crystalline diamide, m. p. 138°.

The bearing of these facts on the nature of plant synthesis is to be discussed in a forthcoming article.

Further researches in connection with the action of *Leuconostoc mesenteroides* and other bacteria (as well as their corresponding enzymes) on carbohydrates are in progress.

PULP AND PAPER RESEARCH INSTITUTE
MCGILL UNIVERSITY
MONTREAL, CANADA
HAROLD HIBBERT
R. STUART TIPSON

RECEIVED MAY 16, 1930
PUBLISHED JUNE 6, 1930

PHENYL URETHAN ANESTHETICS

Sir:

In a recent paper[1] the writer described several phenyl urethan derivatives of dialkyl amino alcohols, and called attention to their great local anesthetic activity. While other compounds of these amino alcohols have not been reported, the activity of the phenyl urethans immediately suggested a study of similar compounds derived from the amino alcohols which are the bases of the popular local anesthetics butyn and novocaine. These compounds were accordingly prepared by the action of phenyl isocyanate on the proper amino alcohol in ether solution. The hydrochlorides were precipitated with gaseous hydrogen chloride and recrystallized from a mixture of acetone and ethyl acetate. The γ-di-*n*-butylaminopropanol phenyl urethan hydrochloride (I) melts at 123–124° (Calcd. for $C_{18}H_{31}O_2N_2Cl$: Cl, 10.4. Found: Cl, 10.1, 10.5), and the β-diethylaminoethanol phenyl urethan hydrochloride (II) melts at 138–139° (Calcd. for $C_{13}H_{21}O_2N_2Cl$: Cl, 13.0. Found: Cl, 12.9). One per cent. aqueous solutions of butyn and novocaine and the corresponding molecular concentrations of the two homologous phenyl urethan hydrochlorides were applied to the cornea of the rabbit for one minute and the durations of the resulting anesthesias were timed. The results are as follows.

Compound	Percentage concentration	Duration of anesthesia of rabbit's cornea, minutes
Butyn	1	25
I	0.96	36
Novocaine	1	Incomplete
II	1	9

Thus both phenyl urethan derivatives produce anesthesias of decidedly longer duration than similar molecular concentrations of their *p*-aminobenzoate homologs. This material although not yet complete demonstrates most convincingly the value of a study of phenyl carbamic acid esters as local anesthetics. A further study is being made of other properties of these compounds and of the general field of phenyl urethan local anesthetics.

LABORATORY OF PHARMACOLOGY AND TOXICOLOGY
YALE UNIVERSITY SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT

T. H. RIDER

RECEIVED MAY 17, 1930
PUBLISHED JUNE 6, 1930

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[1] Rider, THIS JOURNAL, **52**, 2115 (1930).

THE PHOTOCHEMICAL DECOMPOSITION OF NO_2

Sir:

The band spectrum[1] of NO_2 shows regions of diffuse absorption below 3700 Å. and 2448 Å. These have been interpreted by R. Mecke[2] and V. Henri[3] as predissociation spectra. At 3700 Å. the NO_2 should decompose into NO and a normal O atom, whereas at 2448 Å. the oxygen atom should be in a ('D) state. If these statements are correct, then it should be possible to prove chemically the presence of oxygen atoms. Therefore mixtures of NO_2 with H_2, $H_2 + O_2$ and $CO + O_2$ have been exposed to light of various wave lengths.

With light of wave length below 3700 Å., H_2O and CO_2 were formed. From the ratio of the quanta of light absorbed to the amount of water formed it was calculated that the reaction

$$O + H_2 \longrightarrow OH + H$$

proceeds at least 10^4 times as slowly as the reaction

$$O + NO_2 \longrightarrow NO + O_2$$

when the oxygen atom is not excited. With shorter wave lengths (from Cd, Al and Zn sparks) the efficiency of water formation was greater.

From this it may be concluded that in the regions of predissociation oxygen atoms are actually produced. Furthermore, the results obtained confirm the observations of Kistiakowsky,[4] that the probability of a reaction of an O atom with H_2 forming OH + H is small. The experiments with added hydrogen and with added hydrogen and oxygen showed that at room temperature for each hydrogen atom less than two molecules of water are formed.

The details will be given in a paper soon to appear.

Frick Chemical Laboratory
Princeton University
Princeton, New Jersey

Hans-Joachim Schumacher[5]

Received May 19, 1930
Published June 6, 1930

THE ADSORPTION OF COMPLEX AMMONIUM IONS BY SILICA GEL

Sir:

In preparing metallized silica gels by the method of Latshaw and Reyerson,[1] it was early found that complex ammonium salts of platinum and palladium were most easily reduced to the metallic condition by adsorbed hydrogen. On the other hand, the ions of nickel and copper do not reduce

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[1] L. Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[2] R. Mecke, *Die Naturw.*, December 20 (1929); *Z. physik. Chem.*, 7B, 108 (1930).

[3] V. Henri, *Nature*, **125**, 202 (1930).

[4] G. B. Kistiakowsky, This Journal, **52**, 1868 (1930).

[5] International Research Fellow in Chemistry.

[1] Latshaw and Reyerson, This Journal, **47**, 610 (1925).

satisfactorily by the above method. It was, therefore, decided to attempt the reduction of complex salts of copper and nickel by passing hydrogen over silica gel containing these salts. When solutions containing complex cupric ammonium ions were poured on silica gel a surprising result occurred. The complex ammonium ions were found to be very strongly adsorbed by the silica gel. The first liquid which came through the silica gel was almost completely decolorized by the silica gel. The same result was found when complex ammonium ions of nickel were used. When these adsorbed ions are reduced by passing hydrogen over the dried gel an excellent metallic deposit results. The deposit resembles the palladium deposit of the previous method very much. We are continuing the investigation with regard to the specific adsorption of complex ions as well as the use of the metallized gels thus produced.

School of Chemistry
University of Minnesota
Minneapolis, Minnesota

Grant W. Smith
L. H. Reyerson

Received May 26, 1930
Published June 6, 1930

NEW BOOKS

Experimental Physical Chemistry. By Farrington Daniels, J. Howard Mathews and John Warren Williams. McGraw-Hill Book Company, Inc., New York, 1929. xvi + 475 pp. 132 figs. 14.5 × 21 cm. Price, $3.50.

The authors state in their preface that the purposes of this book are "to illustrate the principles of physical chemistry, to train in careful experimentation, to develop familiarity with apparatus, to encourage ability in research." These purposes have led them to divide the material into three sections: Laboratory Experiments (Part I, 285 pp.), Apparatus (Part II, 145 pp.), Miscellaneous Operations (Part III, 29 pp.).

Part I provides a laboratory manual of physical chemistry which is unique both in the number and variety of exercises listed and in the treatment of the individual experiment. One might hope to cover about a third of the 78 experiments in the usual one-year laboratory course. Harassed instructors who want their laboratory outlines ready-made will get little comfort from this book, but others will find its wide scope a convenience where equipment is limited, and a powerful stimulus to the ambitious student. If necessary or desirable, a course of 25 or more exercises may be selected, involving only the conventional types of experiments and simple forms of apparatus. On the other hand, the material is sufficiently extensive to meet the needs of an advanced course such as electrochemistry, or a course introductory to research. Some of the topics covered which are seldom if ever included elsewhere are: viscosity of gases, specific heats of liquids, partial molal volumes, conductance in mixed solvents, decomposition potentials and overvoltage, the manganese